

A structural, infrared, and Mössbauer spectral study of rosemaryite, $\text{NaMnFe}^{3+}\text{Al}(\text{PO}_4)_3$

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Abstract: Rosemaryite, ideally $\text{NaMnFe}^{3+}\text{Al}(\text{PO}_4)_3$, has been collected in the Buranga pegmatite, Rwanda. A single-crystal structure refinement was performed to $R_1 = 4.01\%$, in the $P2_1/n$ space group, with $a = 12.001(2)$, $b = 12.396(1)$, $c = 6.329(1)$ Å, $\beta = 114.48(1)^\circ$, Vol. = $856.9(2)$ Å³, $Z = 4$. The crystal structure and cation distributions are similar to those of ferrosemaryite, $\text{NaFe}^{2+}\text{Fe}^{3+}\text{Al}(\text{PO}_4)_3$, and qingheite, $\text{Na}_2\text{MnMgAl}(\text{PO}_4)_3$, but aluminium predominantly occurs in the M(2a) site, not in the M(2b) site as observed in ferrowyllieite, $\text{Na}_2\text{Fe}^{2+}_2\text{Al}(\text{PO}_4)_3$. The topologies of the X(1a) and X(1b) crystallographic sites are identical to those found in ferrosemaryite, and correspond to a distorted octahedron and to a distorted cube, respectively. The [7+1]-coordinated X(2) site is a very distorted gable disphenoid, similar to the A(2)' site of the alluaudite structure. Mössbauer spectra have been obtained from 4.2 to 295 K, and fitted with a model including two Fe^{3+} and two Fe^{2+} doublets. The Fe^{2+} component corresponding to 2/3 of the Fe^{2+} spectral area and having a smaller quadrupole splitting of 2.63 mm/s at 15 K, is assigned to the Fe^{2+} on the M(2a) site, and the Fe^{2+} component with the larger quadrupole splitting of 3.17 mm/s at 15 K, is assigned to the Fe^{2+} on the M(1) site. Fe^{3+} is located only at the M(2a) and M(2b) sites, and the Fe^{3+} component corresponding to 3/4 of the Fe^{3+} and exhibiting the larger quadrupole splitting of 0.77 mm/s at 15 K, is most likely associated with Fe^{3+} on the M(2b) site. The infrared spectrum of rosemaryite shows absorption bands at 3450 and 1624 cm^{-1} , bands that arise from the vibrational modes of H_2O and confirm the presence of water in the channels of the wyllieite structure. A comparison of both the Mössbauer spectra and structural data of rosemaryite with those of other phosphates of the alluaudite and wyllieite groups, is also presented.

Key-words: Rosemaryite, phosphate mineral, structure refinement, Mössbauer spectroscopy, infrared spectroscopy.

Introduction

The wyllieite group of minerals consists of Na-Mn-Fe-Al-bearing phosphates which exhibit a crystal structure topologically similar to the alluaudite structure (Moore & Molin-Case, 1974). However, the ordering of cations in the wyllieite structure induces a splitting of the M(2) and X(1) sites of alluaudite into the M(2a) M(2b) and X(1a) X(1b) sites. Consequently, the $C2/c$ space group of alluaudite transforms into $P2_1/n$ in wyllieite with no concurrent change in the unit-cell parameters; the corresponding structural formula becomes $\text{X}(2)\text{X}(1a)\text{X}(1b)\text{M}(1)\text{M}(2a)\text{M}(2b)(\text{PO}_4)_3$ (Moore & Molin-Case, 1974).

In granitic pegmatites, particularly in the beryl-columbite-phosphate subtype of the rare-element pegmatites, according to the classification of Černý (1991), wyllieite-type phosphates display chemical compositions ranging from $\text{Na}_2(\text{Mn},\text{Fe}^{2+})\text{Fe}^{2+}\text{Al}(\text{PO}_4)_3$ to $\square\text{Na}(\text{Mn},\text{Fe}^{2+})\text{Fe}^{3+}\text{Al}(\text{PO}_4)_3$, with Ca^{2+} or Mn^{2+} replacing

Na^+ on the X(2), X(1a) and X(1b) sites, Mg^{2+} or Zn^{2+} replacing iron on the M(2a) site, and Mg^{2+} or Fe^{3+} replacing Al^{3+} on the M(2b) site, where \square represents a lattice vacancy (Moore & Ito, 1979). The crystal chemistry of these phosphates has been investigated by Moore & Ito (1979), who proposed a revision of their nomenclature based on chemical data. According to these authors, the name wyllieite corresponds to $\text{Na}_2\text{MnFe}^{2+}\text{Al}(\text{PO}_4)_3$, whereas the name rosemaryite designates the more oxidized compositions, such as $\square\text{NaMnFe}^{3+}\text{Al}(\text{PO}_4)_3$. The prefix ferro- is added if Fe^{2+} dominates in the M(1) site, thus leading to ferrowyllieite, $\text{Na}_2\text{Fe}^{2+}_2\text{Al}(\text{PO}_4)_3$ (Moore & Ito 1979). The name qingheite has been introduced by Zhesheng *et al.* (1983) for the Mg-rich equivalent of wyllieite, $\text{Na}_2\text{MnMgAl}(\text{PO}_4)_3$.

More recently, the new mineral species ferrosemaryite, $\square\text{NaFe}^{2+}\text{Fe}^{3+}\text{Al}(\text{PO}_4)_3$, has been described in the Rubindi pegmatite, Rwanda, and its crystal structure revealed that it belongs to the wyllieite group of minerals, with Al prevailing on the M(2a) site (Hatert *et al.*, 2005a).

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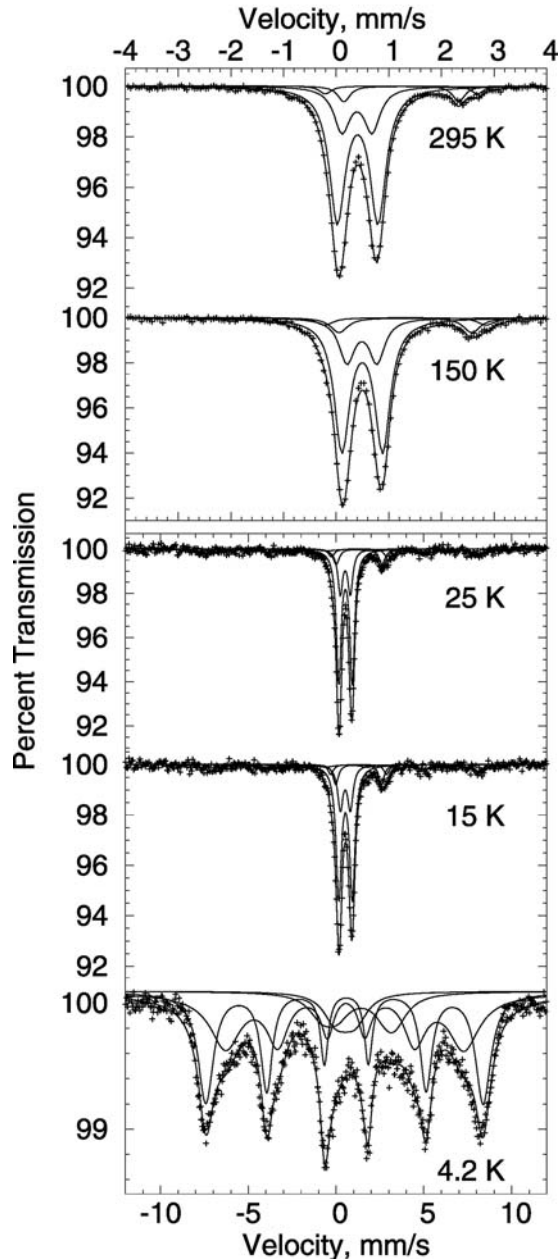


Fig. 1. Mössbauer spectra of rosemaryite from Buranga.

Table 1. Wet chemical analysis of rosemaryite from Buranga (Sample Bu 5.12; Fransolet, 1995).

	1	2
P ₂ O ₅	44.18	3.000
Al ₂ O ₃	8.30	0.785
Fe ₂ O ₃	17.16	1.036
FeO	2.18	0.146
MnO	20.21	1.373
MgO	0.69	0.083
CaO	1.12	0.096
Na ₂ O	3.77	0.586
K ₂ O	0.03	0.003
H ₂ O ⁺	2.36	1.263
Total	100.00	

Analyst: J.-M. Speetjens. The analysis has been recalculated to 100%.

1. Weight %. 2. Number of cations calculated on the basis of 3 P per formula unit.

This unexpected cation distribution, different from that observed in ferrowyllieite by Moore & Molin-Case (1974), was the starting point of this new mineralogical investigation of rosemaryite, collected in the Buranga pegmatite and previously described by Fransolet (1995).

The aim of this study is to perform a single-crystal structure refinement on rosemaryite from Buranga, and to compare its structural data with those obtained for ferrowyllieite (Moore & Molin-Case, 1974), qingheite (Zhesheng *et al.*, 1983), ferrowyllieite (Hatert *et al.*, 2005a), and for the wyllieite-type compound Na_{1.265}Mn²⁺_{2.690}Mn³⁺_{0.785}(PO₄)₃, recently synthesized by Yakubovich *et al.* (2005). A Mössbauer spectral investigation of rosemaryite also permits a comparison with the Mössbauer spectrum of ferrowyllieite (Hatert *et al.*, 2005a), and with the spectra of more disordered alluaudite-type phosphates (Korzynski *et al.*, 1998; Chouaibi *et al.*, 2001; Hermann *et al.*, 2002; Hatert *et al.*, 2003, 2004 and 2005b; Hidouri *et al.*, 2004; Redhammer *et al.*, 2005).

Table 2. The hyperfine parameters obtained from the fits of the Mössbauer spectra between 15 and 295 K.

Relative area ^a	Fe ³⁺						Fe ²⁺				Fe ³⁺ magnetic phase					
	M(2a) 21.9%		M(2b) 65.6%				M(2a) 8.3%		M(1) 4.2%							
	Temperature	Spectral area	δ_{M2a}	$\Delta E_{Q,M2a}$	δ_{M2b}	$\Delta E_{Q,M2b}$	Γ	δ_{M2a}	$\Delta E_{Q,M2a}$	δ_{M1}	$\Delta E_{Q,M1}$	Γ	Fe ³⁺ fraction	H	Γ	ΔE_Q
K	%ε.mm/s	mm/s														
295 ^a	- 8.87	0.41	0.57*	0.40	0.77*	0.37	1.23	2.18	1.24	2.88	0.27	0	-	-	-	-
150	- 9.73	0.50	0.57*	0.49	0.77*	0.35	1.31	2.52	1.32	3.07	0.39	0	-	-	-	-
25	-11.21	0.53	0.57*	0.53	0.77*	0.33	1.36	2.62	1.38	3.15	0.44	17	47.6	1.2	-0.15	
15	-11.11	0.53	0.57*	0.53	0.77*	0.37	1.36	2.63	1.38	3.17	0.43	18	47.7	1.0	-0.18	
4.2	-12.3	- ^b														

^aThe Fe²⁺ has not been constrained for the 295 K spectrum and the fit yields 9.1%. The relative areas for the components are 68.2 and 22.7% for Fe³⁺ on M(2a) and M(2b), respectively, and 6.1 and 3 % for Fe²⁺ on M(2a) and M(1), respectively. For all other temperatures, including 4.2 K, the relative areas have been constrained.

^bSee table 3. * Parameter frozen during refinement.

Table 3. The hyperfine parameters obtained from the 4.2 K Mössbauer spectrum.

	% Area	δ , mm/s	ΔE_Q , mm/s	H, T	Γ , mm/s	$\Delta\Gamma$	θ , °
Fe ³⁺	39(5)	0.534*	0.57*	42.4(7)	0.67(9)	0.21(3)	60(1)
Fe ³⁺	41(5)	0.534*	0.77*	48.9(1)	0.45(3)	0.08(1)	60(1)
Fe ³⁺	8(1)	0.534*	0*	4(1)	1.5(2)	0*	0*
Fe ²⁺	12.5*	1.38*	3.5(1)	4(2)	1.7(3)	0*	97(1)

* Constrained parameter.

Table 4. Experimental details for the single-crystal X-ray diffraction study of rosemeryite from Buranga.

Dimensions of the crystal (mm)	ca. 0.17 × 0.32 × 0.07
<i>a</i> (Å)	12.001(2)
<i>b</i> (Å)	12.396(1)
<i>c</i> (Å)	6.329(1)
β (°)	114.48(1)
Space group	<i>P</i> 2 ₁ / <i>n</i>
Diffractometer	Bruker P4
Operating conditions	50 kV, 30 mA
Radiation	MoK α ($\lambda = 0.71073$ Å)
Scan mode	ω scan
$2\theta_{\max}$	60.8°
Range of indices	$-16 \leq h \leq 16, -1 \leq k \leq 17, -8 \leq l \leq 1$
Measured intensities	3510
Unique reflections	2493
Independent non-zero [$F_o > 4\sigma(F_o)$] reflections	2033
Absorption correction	Semi-empirical
Data reduction program	SHELXTL-Plus (Sheldrick, 1991)
Structure solution program	SHELXS97 (Sheldrick, 1997)
l.s. refinement program	SHELXL97 (Sheldrick, 1997)
Molecular graphics program	ATOMS (Dowty, 1993)
Refined parameters	193
R_1 (on F^2 s) ($F_o > 4\sigma(F_o)$)	0.040
R_1 (all)	0.053
wR_2 (all)	0.102
<i>S</i> (goodness of fit)	1.081
Max Δ/σ in the last l.s. cycle	0.000
Max peak and hole in the final ΔF map ($e/\text{Å}^3$)	+0.87 and -1.66

Table 5. Final fractional coordinates and equivalent isotropic displacement parameters (Å²) for rosemeryite from Buranga.

Site	Atom	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}
X(2)	Na*	-0.0002(5)	-0.0135(6)	0.246(1)	0.032(2)
X(1a)	Mn**	0.5	0	0	0.0442(5)
X(1b)	Na***	0.5	0	0.5	0.032(2)
M(1)	Mn****	0.00274(5)	-0.26107(5)	0.26214(9)	0.0108(2)
M(2a)	Al*****	0.27947(6)	-0.34053(6)	0.3605(1)	0.0071(2)
M(2b)	Fe*****	0.22217(5)	-0.14821(4)	0.62934(9)	0.0075(2)
P(1)	P	0.00354(7)	-0.28313(7)	0.2413(1)	0.0077(2)
P(2a)	P	0.24199(7)	-0.09980(7)	0.1228(1)	0.0085(2)
P(2b)	P	0.24454(7)	0.11190(7)	0.6469(1)	0.0073(3)
O(1a)	O	0.4465(2)	-0.2854(2)	0.5177(4)	0.0111(5)
O(1b)	O	0.4523(2)	-0.7083(2)	0.0450(4)	0.0128(5)
O(2a)	O	0.1062(2)	-0.3509(2)	0.2250(4)	0.0170(5)
O(2b)	O	0.0884(2)	-0.6352(2)	0.7373(4)	0.0157(5)
O(3a)	O	0.3154(2)	-0.3299(2)	0.0893(4)	0.0115(5)
O(3b)	O	0.3340(3)	-0.6571(2)	0.6109(4)	0.0179(5)
O(4a)	O	0.1247(2)	0.4070(2)	0.3415(5)	0.0173(5)
O(4b)	O	0.1172(2)	-0.3999(2)	0.7738(4)	0.0129(5)
O(5a)	O	0.2336(2)	-0.1700(2)	0.3183(4)	0.0141(5)
O(5b)	O	0.2242(2)	-0.8170(2)	0.8299(4)	0.0118(5)
O(6a)	O	0.3114(2)	-0.4879(2)	0.3781(4)	0.0157(5)
O(6b)	O	0.3152(3)	-0.4975(2)	0.8740(5)	0.0199(6)

Refined sites occupancies:

*0.297(10) Na + 0.703(10) □; ****0.930(4) Mn + 0.070(4) □;

0.487(3) Mn + 0.013(3) □; ***0.678(20) Al + 0.325(10) Fe;

0.272(6) Na + 0.228(6) □; **0.737(10) Fe + 0.267(20) Al.

Experimental

Sample selection

The sample, Bu 5.12 from the Buranga pegmatite, Rwanda, investigated herein is the same as that described earlier by Fransolet (1995). The wet chemical analysis of this sample is given in Table 1. The unit-cell parameters, calculated from the X-ray powder diffraction pattern, are $a = 11.977(2)$, $b = 12.388(2)$, $c = 6.320(1)$ Å, and $\beta = 114.45(2)^\circ$. The primitive space group of rosemeryite from Buranga was confirmed by Fransolet (1995) from Weissenberg data.

Mössbauer spectroscopy

The iron-57 Mössbauer spectra of rosemeryite (Fig. 1) were recorded between 4.2 and 295 K on a constant acceleration spectrometer which used a rhodium matrix cobalt-57 source and was calibrated at 295 K with α -iron powder. The isomer shifts reported herein (Tables 2 and 3) are relative to α -iron at 295 K. The Mössbauer spectral absorber contained ca. 18 mg/cm² of powder.

Table 6. Selected bond distances (Å) and angles (°) for rosemaryite from Buranga.

P(1)-O(2a)	1.530(3)	X(2)-O(6a)	2.485(6)
P(1)-O(1b)	1.542(3)	X(2)-O(6b)'	2.515(6)
P(1)-O(2b)	1.545(3)	X(2)-O(6b)	2.659(7)
P(1)-O(1a)	1.545(2)	X(2)-O(1b)	2.697(8)
Mean	1.541	X(2)-O(6a)'	2.707(7)
		X(2)-O(3b)	2.785(7)
O(2a)-P(1)-O(1b)	113.3(1)	X(2)-O(1a)	2.819(8)
O(2a)-P(1)-O(2b)	105.7(2)	X(2)-O(3a)	3.045(8)
O(2a)-P(1)-O(1a)	107.7(1)	Mean	2.714
O(1b)-P(1)-O(2b)	108.4(1)		
O(1b)-P(1)-O(1a)	109.5(2)	X(1a)-O(4b) × 2	2.121(2)
O(2b)-P(1)-O(1a)	112.3(1)	X(1a)-O(2b) × 2	2.207(3)
Mean	109.5	X(1a)-O(4a) × 2	2.412(3)
		Mean	2.247
P(2a)-O(4a)	1.523(3)		
P(2a)-O(6a)	1.527(3)	X(1b)-O(2a) × 2	2.358(3)
P(2a)-O(5a)	1.550(3)	X(1b)-O(4a) × 2	2.359(3)
P(2a)-O(3b)	1.551(3)	X(1b)-O(4b) × 2	2.689(2)
Mean	1.538	X(1b)-O(2b) × 2	2.856(3)
		Mean	2.566
O(4a)-P(2a)-O(6a)	111.3(2)		
O(4a)-P(2a)-O(5a)	109.0(1)	M(1)-O(1a)	2.176(2)
O(4a)-P(2a)-O(3b)	109.5(2)	M(1)-O(4b)	2.194(3)
O(6a)-P(2a)-O(5a)	110.3(2)	M(1)-O(1b)	2.213(3)
O(6a)-P(2a)-O(3b)	109.4(1)	M(1)-O(4a)	2.249(3)
O(5a)-P(2a)-O(3b)	107.3(1)	M(1)-O(3b)	2.252(3)
Mean	109.5	M(1)-O(3a)	2.284(3)
		Mean	2.228
P(2b)-O(6b)	1.514(3)		
P(2b)-O(4b)	1.529(3)	M(2a)-O(6a)	1.860(3)
P(2b)-O(3a)	1.543(2)	M(2a)-O(2a)	1.897(3)
P(2b)-O(5b)	1.553(3)	M(2a)-O(3a)	1.940(3)
Mean	1.535	M(2a)-O(1a)	1.955(2)
		M(2a)-O(5b)	2.000(3)
O(6b)-P(2b)-O(4b)	110.7(2)	M(2a)-O(5a)	2.173(3)
O(6b)-P(2b)-O(3a)	108.7(1)	Mean	1.971
O(6b)-P(2b)-O(5b)	111.0(2)		
O(4b)-P(2b)-O(3a)	111.7(1)	M(2b)-O(6b)	1.920(3)
O(4b)-P(2b)-O(5b)	107.1(1)	M(2b)-O(3b)	2.022(3)
O(3a)-P(2b)-O(5b)	107.6(1)	M(2b)-O(5a)	2.047(3)
Mean	109.5	M(2b)-O(1b)	2.060(3)
		M(2b)-O(2b)	2.077(3)
		M(2b)-O(5b)	2.172(3)
		Mean	2.050

Infrared spectroscopy

The infrared spectrum of rosemaryite (Fig. 2) was recorded with a Nicolet NEXUS spectrometer, from 32 scans with a 1 cm⁻¹ resolution, between 400 and 4000 cm⁻¹. The sample was prepared by thoroughly mixing 2 mg of sample with KBr in order to obtain a 150 mg homogeneous pellet which was subsequently dried for several

hours at 120°C. To prevent water contamination, the measurements were performed under a dry air purge.

Structure refinement

The X-ray structural study was carried out on a Bruker P4 four-circle diffractometer (MoK_α radiation, λ = 0.71073 Å), on a crystal fragment of 0.17 × 0.32 × 0.07 mm. The unit-cell parameters and standard deviations were calculated for the setting angles of 37 reflections with 9.8° < 2θ < 24.9°: a = 12.001(2), b = 12.396(1), c = 6.329(1) Å, and β = 114.48(1)°. The intensities of 3510 reflections, corresponding to 2493 unique reflections (R_{int.} = 0.037), were measured by the ω scan technique in the range 3.3° < 2θ < 60.8° (h = $\overline{16} \rightarrow 16$, k = $\overline{1} \rightarrow 17$, l = $\overline{8} \rightarrow 1$). Data were corrected for Lorentz polarization and absorption effects, the latter with a semi-empirical method using a reliable set of ψ-scan data (North *et al.*, 1968).

The crystal structure was refined in space group P2₁/n, which was confirmed from systematic absences. The starting atomic coordinates were those of ferrowyllieite (Moore & Molin-Case, 1974), and scattering curves for neutral atoms, together with anomalous dispersion corrections, were taken from *International Tables for X-ray Crystallography, Vol. C* (Wilson, 1992). Cation occupancies were refined to obtain better agreement with the chemical composition of rosemaryite (Table 1). For simplicity, Ca²⁺ and Mg²⁺, which are present in very low amounts, were not taken into account in the crystal structure refinement. Finally, the relative occupancies of Fe³⁺ and Al³⁺ on the M(2a) and M(2b) sites, of Mn²⁺ and vacancies on the X(1a) and M(1) sites, and of Na⁺ and vacancies on the X(2) and X(1b) sites, were refined. The refinement was completed using anisotropic displacement parameters for all atoms. The final conventional R_f factor was 0.040. Further details of the intensity data collection and refinement are given in Table 4.

Final positional and isotropic thermal parameters for rosemaryite are given in Table 5, and selected bond distances and angles are given in Table 6. Anisotropic thermal parameters are available from the authors or through the EJM editorial office – Paris.

Mössbauer spectroscopy

Model

The general appearance of the Mössbauer spectra obtained between 15 and 295 K indicates that they should be fit with at least two doublets, one with a small isomer shift and quadrupole splitting assigned to Fe³⁺, and one with a large isomer shift and quadrupole splitting assigned to Fe²⁺ (Fig. 1). However, both the poor fits and the broad lines obtained from preliminary fits reveal that an acceptable fit will require at least two Fe³⁺ doublets and two Fe²⁺ doublets. Such four doublet fits, with no constraints on the hyperfine parameters, indicate both that the 12.5 % Fe²⁺ fraction is essentially independent of temperature below 150 K and that the quadrupole splittings of both Fe³⁺

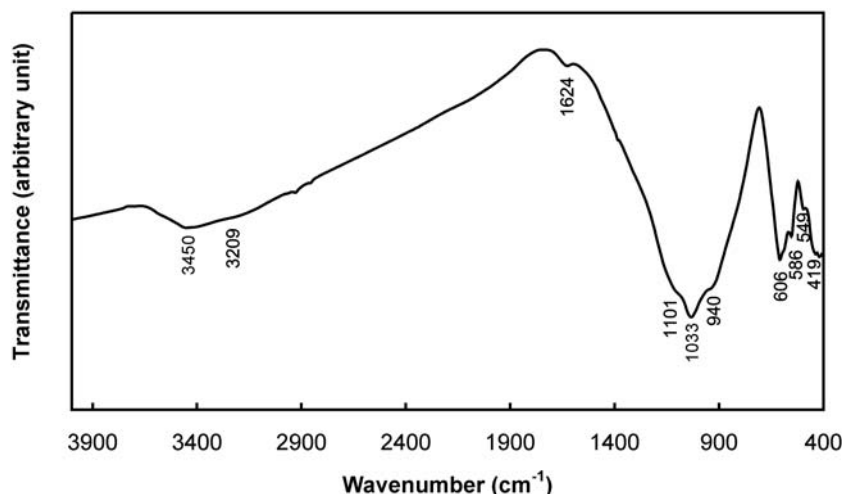


Fig. 2. Infrared spectrum of rosemaryite from Buranga.

Table 7. Refined site populations (RSP, *apfu*), refined site-scattering values (RSS, *epfu*), mean bond-lengths (MBL, Å), assigned site populations (ASP, *apfu*), calculated site-scattering values (CSS, *epfu*), and calculated bond lengths (CBL, Å) for rosemaryite from Buranga.

Site	Results of the structure determination			Results of the chemical analysis		
	RSP	RSS	MBL	ASP	CSS	CBL*
X(2)	0.297 Na	3.3	2.667**	0.436 Na ⁺	4.8	2.600
X(1a)	0.487 Mn	12.2	2.247	0.450 Mn ²⁺ + 0.050 Na ⁺	11.8	2.249
X(1b)	0.272 Na	3.0	2.566	0.100 Na ⁺ + 0.069 Mn ²⁺	2.8	2.510
M(1)	0.930 Mn	23.3	2.228	0.754 Mn ²⁺ + 0.096 Ca ²⁺ + 0.083 Mg ²⁺ + 0.067 Fe ²⁺	23.5	2.234
M(2a)	0.678 Al + 0.325 Fe	17.3	1.971	0.685 Al ³⁺ + 0.236 Fe ³⁺ + 0.079 Fe ²⁺	17.1	1.980
M(2b)	0.737 Fe + 0.267 Al	22.6	2.050	0.800 Fe ³⁺ + 0.100 Al ³⁺ + 0.100 Mn ²⁺	24.6	2.053

*: The CBL values have been calculated from the ASP, assuming a full occupancy of the crystallographic sites.

** : For the calculation of the X(2)-O MBL, the very long X(2)-O(3a) bond has not been taken into account.

Table 8. Bond-valence table (vu) for rosemaryite from Buranga.

	X(2)	X(1a)	X(1b)	M(1)	M(2a)	M(2b)	P(1)	P(2a)	P(2b)	Σ
O(1a)	0.064			0.357	0.479		1.215			2.12
O(1b)	0.089			0.323		0.434	1.225			2.07
O(2a)			0.220 *		0.561		1.265			2.05
O(2b)		0.325 *	0.057 *			0.415	1.215			2.01
O(3a)	0.035			0.267	0.499				1.221	2.02
O(3b)	0.070			0.291		0.481		1.195		2.04
O(4a)		0.187 *	0.219 *	0.293				1.289		1.99
O(4b)		0.410 *	0.090 *	0.340					1.269	2.11
O(5a)					0.266	0.450		1.199		1.92
O(5b)					0.425	0.321			1.189	1.94
O(6a)	0.245				0.620			1.275		2.14
O(6b)	0.245					0.634			1.321	2.20
S _{calc.}	0.75	1.84	1.17	1.87	2.85	2.73	4.92	4.96	5.00	
S _{theor.}	1.00	1.90	1.41	2.00	2.92	2.90	5.00	5.00	5.00	

The bond valences were calculated from the bond lengths given in Table 6, and from the assigned site populations of Table 7, with the parameters of Brown & Altermatt (1985). *: Bond valences were multiplied by two, for the calculation of the valence on the X(1a) and X(1b) crystallographic sites. A full occupancy has been assumed for the X(2) and X(1b) sites.

components are temperature independent within their error limits. Further, essentially temperature independent ratios of 2:1 and 3:1 were observed for the areas of the two Fe³⁺

and two Fe²⁺ components, respectively. Thus for the final fits, the Fe²⁺ content has been constrained to 12.5 % of the total iron and, for the Fe³⁺ doublets, constrained quadrupole

splittings of 0.772 and 0.571 mm/s have been used for the components with relative areas of 1/3 and 2/3, respectively. In contrast, for the Fe²⁺ doublets, constrained relative areas of 1/4 and 3/4 have been used for the components with the small and large quadrupole splittings, respectively. At 15 and 25 K a weak magnetic sextet is observed with a hyperfine field of ~48 T; the area of this sextet must be added to the Fe³⁺ fraction in order to ensure a constant Fe²⁺ content at low temperature.

The final fit of the 150 K spectrum involved the adjustment of 10 parameters, four isomer shifts, δ , two Fe²⁺ quadrupole splittings, ΔE_Q , two line widths, Γ , one each for the Fe²⁺ and Fe³⁺ components, as well as the total spectral area and spectral baseline. In addition, for the 295 K spectrum, the Fe²⁺ content has been varied and, for the 15 and 25 K spectra, four additional parameters, the area, the hyperfine field, the quadrupole interaction, and the line width of the broad sextet, have been varied. The isomer shift of this sextet was constrained to 0.53 mm/s, the average of the Fe³⁺ isomer shifts at higher temperature.

The Mössbauer spectrum measured at 4.2 K indicates the presence of long range magnetic hyperfine interactions. The relatively large absorption at -6 and +6.5 mm/s indicates the presence of two different contributions, with rather large magnetic hyperfine fields that can be assigned to Fe³⁺. Because the absorption at 2.5 mm/s is much smaller at 4.2 than at 15 K, the Fe²⁺ components associated with the absorption at this velocity at 15 K must also be magnetically split at 4.2 K, although with a smaller hyperfine magnetic field. Because the Fe²⁺ quadrupole and magnetic hyperfine interactions are similar, a fit of the 4.2 K spectrum requires the diagonalization of the Hamiltonian. Thus the fit has used a three magnetic component model with one Fe²⁺ and two Fe³⁺ sextets plus an additional small Fe³⁺ component, with a large line width and a small hyperfine field. The latter component is required to fit the incomplete magnetic ordering at 4.2 K. A comparison with other spectra obtained for alluaudites indicate that the 4.2 K spectrum of rosemaryite is similar to the incompletely ordered alluaudite spectrum of natural NaMnFe₂(PO₄)₃ obtained at 15 K (Hatert *et al.*, 2004). Apparently complete magnetic ordering in rosemaryite occurs below 4.2 K. Except for the 12.5 % Fe²⁺ content, the relative spectral absorption areas of the spectral components have not been constrained to those of the paramagnetic spectra. The isomer shifts obtained at 15 K have been used at 4.2 K in order to reduce the number of free parameters; the quadrupole interactions observed at 15 K have been constrained for the two Fe³⁺ magnetic components and allowed to vary for the Fe²⁺ component; the resulting value was consistent with the higher temperature values. Unfortunately, field distributions prevent the attribution of the magnetic components to a specific site. Further, an incremental broadening parameter, $\Delta\Gamma$, was introduced for the two Fe³⁺ components in order to mimic a distribution of the hyperfine fields that results from variations in the local environment; the line width at a given velocity, v , relative to the isomer shift, δ , of a component is then given by $\Gamma + \Delta\Gamma \cdot \text{abs}(v - \delta)$. The hyperfine parameters obtained from the final fits are given in Tables 2 and 3.

Site assignment

The iron ions in rosemaryite are located on three M(1), M(2a), and M(2b) sites. A possible assignment of the two Fe³⁺ and the two Fe²⁺ components to specific sites can be obtained through a comparison with an earlier Mössbauer spectral study of ferrosemaryite (Hatert *et al.*, 2005a). In ferrosemaryite, Fe²⁺ is located on the M(1) and M(2a) sites and the quadrupole splitting of ~3.3 mm/s for the Fe²⁺ on the M(1) site is much larger than the splitting of ~2.3 mm/s for the Fe²⁺ on the M(2a) site. In rosemaryite, it is thus reasonable to attribute the Fe²⁺ component that corresponds to 2/3 of the Fe²⁺ spectral area and has the smaller quadrupole splitting of 2.63 mm/s at 15 K, to Fe²⁺ on the M(2a) site, and the Fe²⁺ component with the larger quadrupole splitting of 3.17 mm/s at 15 K, to Fe²⁺ on the M(1) site. In ferrosemaryite, Fe³⁺ is located on three sites and the more distorted M(1) site corresponds to the larger quadrupole splitting of 1.03 mm/s. Because no Fe³⁺ component with such a large quadrupole splitting is observed in the rosemaryite Mössbauer spectra, Fe³⁺ is most likely found only on the M(2a) and M(2b) sites. In ferrosemaryite, the M(2b) site accommodates most of the Fe³⁺ and corresponds to the larger quadrupole splitting of ~0.74 mm/s; in rosemaryite, the Fe³⁺ component with the larger spectral area, 3/4 of the Fe³⁺, also exhibits the larger quadrupole splitting, and can most likely be assigned to Fe³⁺ on the M(2b) site. The hyperfine parameters of the smaller area component, 1/4 of the Fe³⁺, are close to those observed for Fe³⁺ on M(2a) in ferrosemaryite in which δ is 0.51 mm/s and ΔE_Q is 0.52 mm/s at 85 K and, thus, the assignment of the smaller area component to Fe³⁺ on M(2a) seems reasonable.

The incremental broadening discussed above and shown in Fig. 1 is not unreasonable because the variety of the near-neighbour environments on the M(2a) and M(2b) sites will yield a distribution of hyperfine fields. However, the relative areas of the spectral lines of the magnetic sextets have been constrained to the usual 3:2:1:1:2:3 ratio. Because of the distribution of cations on the different sites, the hyperfine parameters obtained on the Fe²⁺ are less reliable but do provide an indication of the magnitude of the correct hyperfine interactions (Table 3).

Infrared spectroscopy

The infrared spectrum of rosemaryite (Fig. 2) is similar to those of alluaudite-type phosphates (Antenucci *et al.*, 1993; Hatert *et al.*, 2002, 2003, 2005b) and of ferrosemaryite (Hatert *et al.*, 2005a), with stretching vibrational modes of the PO₄ tetrahedra in the 1200 to 850 cm⁻¹ region, PO₄ bending vibrational modes between *ca.* 400 and 650 cm⁻¹, and lattice vibrations at lower frequencies.

It is important to note the large absorption band found at 3450 cm⁻¹ (Fig. 2), a band that is related to the O-H stretching vibrational mode (Farmer, 1974). The presence of protons in natural alluaudites has been suspected by Franolet *et al.* (1994) on the basis of wet chemical analyses, and the synthetic protonated alluaudite-type

compounds $M^+M^{2+}_3(\text{PO}_4)(\text{HPO}_4)_2$, where M^+ is Na^+ or Ag^+ and M^{2+} is Mn^{2+} or Co^{2+} , have been synthesized by Lii & Shih (1994), Leroux *et al.* (1995a and b) and Guesmi & Driss (2002). More recently, single-crystal X-ray diffraction and infrared spectroscopic investigations of the new arsenate mineral, yazganite, $\text{NaFe}^{3+}_2(\text{Mg},\text{Mn})(\text{AsO}_4)_3\cdot\text{H}_2\text{O}$, have demonstrated the existence of molecular water localized in channel 2 of the alluaudite structure, at position 0.003(1), 0.0004(4), 0.272(2) (Sarp & Černý, 2005).

The rosemaryite infrared absorption band at 1624 cm^{-1} (Fig. 2), is assigned to the bending vibrational mode of H_2O , and its observation confirms the presence of molecular water in the channels of the wylieite structure. According to the wet chemical analysis (Table 1), the H_2O content of rosemaryite from Buranga reaches 0.63 molecules per formula unit, and the formula of this mineral corresponds to $(\square_{0.88}\text{Na}_{0.12})(\text{Na}_{0.47}\text{Ca}_{0.10}\text{Mn}_{0.43})(\text{Mn}_{0.94}\text{Fe}^{2+}_{0.06})(\text{Fe}^{3+}_{0.83}\text{Fe}^{2+}_{0.09}\text{Mg}_{0.08})(\text{Al}_{0.79}\text{Fe}^{3+}_{0.21})(\text{PO}_4)_3\cdot 0.63\text{H}_2\text{O}$. In the infrared spectrum of ferrosemaryite (Hatert *et al.*, 2005a), an absorption band was observed at 3375 cm^{-1} , but without any absorption band around 1600 cm^{-1} . Consequently, these authors tentatively assigned the band at 3375 cm^{-1} to the stretching vibrations of OH^- groups localised at the apex of an HPO_4^{2-} tetrahedron, but this assignment probably should be revised in view of the better quality of the infrared data obtained for rosemaryite.

Structure refinement

The basic features of the rosemaryite structure are identical to those of the other members of the wylieite group (Moore & Molin-Case, 1974; Zhesheng *et al.*, 1983; Yakubovich *et al.*, 2005; Hatert *et al.*, 2005a). The structure consists of kinked chains of edge-sharing octahedra stacked parallel to $\{101\}$. These chains are formed by a succession of M(2a)–M(2b) octahedral pairs, linked by highly distorted M(1) octahedra. Equivalent chains are connected in the b direction by the P(1), P(2a), and P(2b) phosphate tetrahedra to form sheets oriented perpendicular to $[010]$. These interconnected sheets produce channels parallel to c , channels that contain the large X sites.

A detailed cationic distribution has also been established, by taking into account the results of the chemical analyses, of the Mössbauer spectral study, and of the single-crystal structure refinement. The results given in Table 7 indicate that the refined site populations (RSP), obtained from the single-crystal structure refinement (Table 5), are in good agreement with the assigned site populations (ASP), deduced from the chemical and Mössbauer spectral results. Moreover, the refined site scattering values (RSS) and the mean bond lengths (MBL), obtained from the structure refinement, are very close to the calculated site scattering values (CSS) and the calculated bond lengths (CBL), respectively (Table 7). This agreement confirms the reliability of the assigned site populations.

The bond valence table for ferrosemaryite is given in Table 8, where the bond valence sums were calculated as $s = \exp[(R_\theta - R)/0.37]$, by using the R_θ values of Brown &

Altermatt (1985). The bond valences for oxygen are close to the theoretical value of 2.00, and the bond valences for phosphorus are very close to the theoretical value of 5.00 (Table 8). For all the cationic sites, a good correspondence between the theoretical and the calculated valence values is generally observed.

Finally, bond length distortion (BLD) and bond angle distortion (BAD) parameters were calculated for the M sites of the rosemaryite structure, with a method modified from Renner & Lehmann (1986) and already used by Hatert *et al.* (2004). The distortion parameters are much higher for the M(1) site (BLD = 1.51; BAD = 14.28) than for M(2a) (BLD = 0.40; BAD = 7.38) and M(2b) (BLD = 0.31; BAD = 9.85), thus confirming the site assignments proposed for the interpretation of the Mössbauer spectra (see above).

Discussion

The crystal structure and cation distribution of wylieite-type phosphates

In addition to an unpublished diploma thesis (Brier, 2000), only three crystal structure refinements on wylieite-type minerals have been reported, one for ferrowylieite (Moore & Molin-Case, 1974), a second for qingheite (Zhesheng *et al.*, 1983), and a third for ferrosemaryite (Hatert *et al.*, 2005a). The mean M–O bond lengths and the cation distributions among the different crystallographic sites of these minerals are given in Table 9, and compared with the data obtained by Yakubovich *et al.* (2005) on the synthetic wylieite-type compound, $\text{Na}_{1.265}\text{Mn}^{2+}_{2.690}\text{Mn}^{3+}_{0.785}(\text{PO}_4)_3$.

A careful examination of the atomic coordinates reported by Zhesheng *et al.* (1983) indicate that the M(2a)–M(2b) and X(1a)–X(1b) pairs of crystallographic sites, which result from a splitting of the M(2) and X(1) sites of the alluaudite structure, have been inverted in qingheite. Atomic coordinates similar to those given by Moore & Molin-Case (1974) can be obtained by applying the translation $x, y - 0.5, z - 0.5$. For consistency, the names used for the crystallographic sites of qingheite by Zhesheng *et al.* (1983) have been inverted in Table 9 and in the following discussion.

Compared to ferrowylieite and qingheite, ferrosemaryite and rosemaryite are highly oxidized, and consequently contain a significant number of vacancies per formula unit. For this reason, in ferrosemaryite, the X(2) site is unoccupied, and the X(1b) site contains 0.310(4) vacancies per formula unit (Hatert *et al.*, 2005a). In rosemaryite, the X(2) site contains 0.703(10) vacancies per formula unit, whereas X(1a) and X(1b) contain 0.013(3) and 0.228(6) vacancies per formula unit, respectively (Table 5).

The X(1a) site of rosemaryite is shown in Fig. 3a, and corresponds to a very distorted octahedron, while the X(1b) site (Fig. 3b) can be described as a very distorted cube. The topologies of these sites are identical to those described in qingheite and ferrosemaryite (Zhesheng *et al.*

Table 9. Comparison of the unit-cell parameters, assigned site populations (ASP, *apfu*), and mean bond lengths (MBL, Å) for wyllieite-type phosphates.

	Ferrowyllieite	Ferrorosemaryite	Rosemaryite	Qingheite	Synthetic compound
References	1	2	3	4	5
Ideal formula	Na ₂ Fe ²⁺ ₂ Al(PO ₄) ₃	□NaFe ²⁺ Fe ³⁺ Al(PO ₄) ₃	□NaMn ²⁺ Fe ³⁺ Al(PO ₄) ₃	Na ₂ MnMgAl(PO ₄) ₃	Na ₂ Mn ²⁺ ₂ Mn ³⁺ (PO ₄) ₃
Space group	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> (Å)	11.868(15)	11.838(1)	12.001(2)	11.856(3)	6.5291(6)
<i>b</i> (Å)	12.382(12)	12.347(1)	12.396(1)	12.411(3)	12.653(1)
<i>c</i> (Å)	6.354(9)	6.2973(6)	6.329(1)	6.421(1)	10.952(1)
β (°)	114.52(8)	114.353(6)	114.48(1)	114.45(2)	97.18(1)
M(2a) ASP	1.00Fe ²⁺	0.72Al ³⁺ + 0.14Fe ²⁺ + 0.14Fe ³⁺	0.69Al ³⁺ + 0.24Fe ³⁺ + 0.08Fe ²⁺	0.42Al ³⁺ + 0.26Fe ²⁺ + 0.18Mg ²⁺ + 0.13Fe ³⁺ + 0.01Zn ²⁺	1.00Mn ²⁺
MBL	2.098	1.963	1.971	2.001	2.164
M(2b) ASP	0.75Al ³⁺ + 0.25Fe ²⁺	0.88Fe ³⁺ + 0.10Al ³⁺ + 0.02Mg	0.80Fe ³⁺ + 0.10Al ³⁺ + 0.10Mn ²⁺	0.95Mg ²⁺ + 0.05Mn ²⁺	0.79Mn ³⁺ + 0.21Mn ²⁺
MBL	1.973	2.019	2.050	2.092	2.046
M(1) ASP	0.75Fe ²⁺ + 0.25Mg ²⁺	0.57Fe ²⁺ + 0.20Fe ³⁺ + 0.18Na ⁺ + 0.05Mn ²⁺	0.75Mn ²⁺ + 0.10Ca ²⁺ + 0.08Mg ²⁺ + 0.07Fe ²⁺	1.00Mn ²⁺	1.00Mn ²⁺
MBL	2.225	2.175	2.228	2.221	2.235
X(1a) ASP	0.46Na ⁺ + 0.04 □	0.43Mn ²⁺ + 0.07Na ⁺	0.45Mn ²⁺ + 0.05Na ⁺	0.50Mn ²⁺	0.41Na ⁺ + 0.09 □
MBL	2.533	2.255	2.247	2.242	2.602
X(1b) ASP	0.25Ca ²⁺ + 0.25Mn ²⁺	0.17Na ⁺ + 0.04Mn ²⁺ + 0.04Ca ²⁺ + 0.25 □	0.10Na ⁺ + 0.07Mn ²⁺ + 0.33 □	0.50Na ⁺	0.48Mn ²⁺ + 0.02 □
MBL	2.209	2.543	2.566	2.541	2.279
X(2) ASP	0.70Na ⁺ + 0.30 □	1.0 □	0.44Na ⁺ + 0.56 □	0.81Na ⁺ + 0.08Ca ²⁺ + 0.11 □	0.85Na ⁺ + 0.15 □
MBL	2.723	-	2.667	2.732	2.635

1. Moore & Molin-Case (1974); 2. Hatert *et al.* (2005a); 3. This paper; 4. Zhesheng *et al.* (1983); 5. Yakubovich *et al.* (2005). For qingheite, the M(2a)-M(2b) and X(1a)-X(1b) pairs of crystallographic sites have been inverted.

al., 1983; Hatert *et al.*, 2005a), but, in ferrowyllieite and in synthetic Na_{1.265}Mn²⁺_{2.690}Mn³⁺_{0.785}(PO₄)₃, X(1a) is better described as a distorted cube and X(1b) as a distorted octahedron (Moore & Molin-Case, 1974; Yakubovich *et al.*, 2005). This change in topology for the X(1b) site probably results from the splitting of this site from its inversion centre in ferrowyllieite and in the synthetic compound, but not in ferrorosemaryite and rosemaryite (Table 5). It is also noteworthy that the topology of the cubic X(1b) site of rosemaryite is similar to the topology of the X(1) site in the alluaudite structure (Antenucci *et al.*, 1995; Hatert *et al.*, 2000).

The X(2) site is described by Moore & Molin-Case (1974) as a highly distorted square antiprism with two supplementary very long distances of 3.58 and 3.62 Å, and by Yakubovich *et al.* (2005) as a trigonal prism with one additional oxygen near the side face. As shown in Table 6, the X(2) site in rosemaryite clearly shows a [7+1] coordination, with 7 “short” bonds ranging from 2.485 to 2.819 Å, and one supplementary very long X(2)–O(3a) bond of 3.045 Å. The coordination polyhedra is shown in Fig. 3c, and can be described as a very distorted gable disphenoid, similar to that observed for the A(2)’ site in the alluaudite structure (Hatert *et al.*, 2000).

As already noted by Hatert *et al.* (2005a) for ferrorosemaryite, the distributions of Fe³⁺ and Al³⁺ between the

M(2a) and M(2b) crystallographic sites in rosemaryite and qingheite are different from that occurring in ferrowyllieite (Table 9). In ferrowyllieite and in synthetic Na_{1.265}Mn²⁺_{2.690}Mn³⁺_{0.785}(PO₄)₃, the very large Fe²⁺ and Mn²⁺ cations, with effective ionic radii of 0.780 and 0.830 Å, respectively (Shannon, 1976), preferentially occupy the M(2a) site, while Al³⁺, with an effective ionic radius of 0.535 Å, preferentially occupies the M(2b) site. In ferrorosemaryite, rosemaryite, and qingheite, the difference in ionic radii between the cations occupying the M(2a) and M(2b) sites decreases, thus leading to a different cation distribution in which Al³⁺ predominates on the M(2a) site and Fe³⁺ or Mg²⁺, with effective ionic radii of 0.645 and 0.720 Å, respectively, occupy the M(2b) site (Table 9). The affinity of Fe³⁺ for the M(2b) site also explains the presence of Mn³⁺ on this site in the wyllieite-type compound synthesized by Yakubovich *et al.* (2005), because the 0.645 Å effective ionic radius of Mn³⁺ (Shannon, 1976) is identical to that of Fe³⁺.

The different cation distributions between the M(2a) and M(2b) sites also slightly affect the X-sites occupancies. As is indicated in Table 9, the X(1a) site predominantly contains Na⁺ in ferrowyllieite and in the synthetic compound, while it contains Mn²⁺ in ferrorosemaryite, rosemaryite, and qingheite. In contrast, X(1b) is occupied by Na⁺ in ferrorosemaryite, rosemaryite, and qingheite,

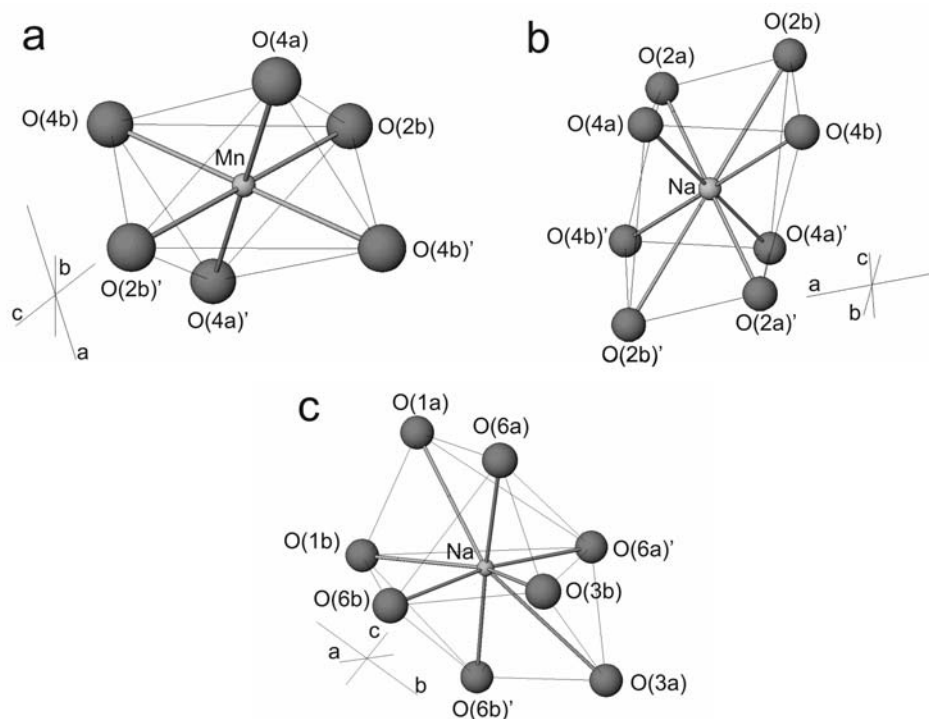


Fig. 3. The X(1a) (a), X(1b) (b) and X(2) (c) crystallographic sites of rosemaryite.

whereas Mn^{2+} and Ca^{2+} occupy the X(1b) site of ferrowyllieite and of the synthetic compound. The X(2) site generally accommodates Na^+ and vacancies, sometimes with minor amounts of Mn^{2+} or Ca^{2+} .

Mössbauer spectra of wylieite- and alluaudite-type phosphates

Over the past decade, numerous alluaudite-type phosphates have been synthesized by solid-state reactions or by hydrothermal techniques; see Hatert *et al.* (2000), Hatert (2002), and Hatert (2004) for a recent review of this literature. The synthesis of pure alluaudites has made possible a detailed investigation of the distribution of cations in the alluaudite structure (Antenucci, 1992; Hatert, 2002). In addition, Mössbauer spectral studies of alluaudites (Korzenski *et al.*, 1998; Chouaibi *et al.*, 2001; Hermann *et al.*, 2002; Hatert *et al.*, 2003, 2004 and 2005b; Hidouri *et al.*, 2004; Redhammer *et al.*, 2005) have revealed the existence of next-nearest neighbour interactions between the iron ions found in the octahedral sites of the structure.

The hyperfine parameters obtained for rosemaryite and ferrowyllieite (Hatert *et al.*, 2005a) are similar to those reported for alluaudite-type phosphates. The isomer shifts and quadrupole splittings at 85 K are in the range of 0.51 to 0.55 mm/s and 0.45 to 1.15 mm/s for Fe^{3+} and 1.29 to 1.38 mm/s and 2.30 to 3.25 mm/s for Fe^{2+} , respectively. The iron ions generally occupy the M(2) site, except in ferrowyllieite, rosemaryite, and the synthetic alluaudite-type $\text{Na}_2(\text{Mn}_{1-x}\text{Fe}^{2+x})_2\text{Fe}^{3+}(\text{PO}_4)_3$ compounds, with $x = 0.75$ and 1.00, (Hatert *et al.*, 2005b), in which iron also occurs at the M(1) site. The 3.13 and 3.284 mm/s

quadrupole splittings observed at 85 K for Fe^{2+} on the M(1) site in rosemaryite and ferrowyllieite are higher than the 3.035 to 3.060 mm/s values observed in synthetic alluaudites, thus indicating that the M(1) site in wylieites is probably more distorted than in alluaudites.

Finally, it is noteworthy that the Mössbauer spectra of alluaudites and wylieites are extremely similar and show little significant variation induced by the splitting of the M(2) site into the M(2a) and M(2b) sites. The next-nearest neighbour interactions around the iron ions are similar in these two structure-types, and the use of Mössbauer spectroscopy, which is a local probe, to evaluate the environment of these iron ions, does not reveal any significant differences between these minerals. The ordering of cations, which induces the splitting of the M(2) site into the M(2a) and M(2b) sites on the larger scale of the unit-cell, is within the investigative range of X-ray diffraction but not of Mössbauer spectroscopy.

Stability of wylieite- and alluaudite-type phosphates, and the role of aluminium

According to Moore & Ito (1973) and Moore & Molin-Case (1974), the occurrence of significant amounts of aluminium in the wylieite structure, and not in the alluaudites, is responsible for the splitting of the M(2) site. They propose that this splitting occurs because Al^{3+} has a very small effective ionic radius of 0.535 Å (Shannon, 1976), as compared to the 0.780 and 0.645 Å ionic radii of Fe^{2+} and Fe^{3+} , respectively.

Recently, Al-rich phosphates with the nominal $\text{Na}_2\text{Mn}_2\text{Al}(\text{PO}_4)_3$ composition have been hydrothermally

synthesized at 300 to 800°C and 1 to 5 kbar (Hatert, 2002). Between 300 and 600°C, white powders without visible crystals were obtained, and the powder X-ray diffraction patterns correspond to those of alluaudite-type phosphates, without any of the supplementary reflections typical of the $P2_1/n$ wyllieite space group. As discussed by Hatert *et al.* (2005a), however, the identification of wyllieite-type phosphates can only be confirmed by single-crystal X-ray diffraction techniques. At 700°C/3.5 kbar and 800°C/1 kbar, tiny acicular crystals were obtained, and single-crystal structure refinements indicated an alluaudite-type structure (Hatert, 2006). Consequently, it appears that the presence of significant amounts of aluminium in the alluaudite structure is not the only parameter which induces the splitting of the M(2) site and the crystallization of wyllieite.

The synthesis of the wyllieite-type phosphate $\text{Na}_{1.265}\text{Mn}^{2+}_{2.690}\text{Mn}^{3+}_{0.785}(\text{PO}_4)_3$, at 400°C and 0.1 kbar (Yakubovich *et al.*, 2005), force us to conclude that aluminium is not necessary to stabilize the wyllieite structure, and that wyllieite-type phosphates crystallize at lower temperatures than alluaudites. This last result is contradictory to the hypothesis of Moore & Ito (1973) and Moore & Molin-Case (1974), who indicated that ferrowyllieite is of primary origin, whereas alluaudites are secondary.

Because of their highly versatile structure, alluaudite-type phosphates are able to crystallize under various temperature and pressure conditions, and their origin in granitic pegmatites can be primary or secondary (Hatert, 2002, 2004; Fransolet *et al.*, 2004). But the ordering responsible for the crystallization of wyllieite-type phosphates seems to occur over a narrow range of temperature and pressure. When cations with very different effective ionic radii occupy the M(2) site, low temperatures can induce the crystallisation of ordered wyllieites, whereas high temperatures induce the disordered cation distribution leading to the crystallisation of alluaudite (Hatert, 2002, 2006). Further experimental investigations, starting from the $\text{Na}_2\text{Mn}_2\text{Al}(\text{PO}_4)_3$ composition, are necessary to obtain single-crystal data well below 700°C and to eventually detect the presence of wyllieite-type phosphates.

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